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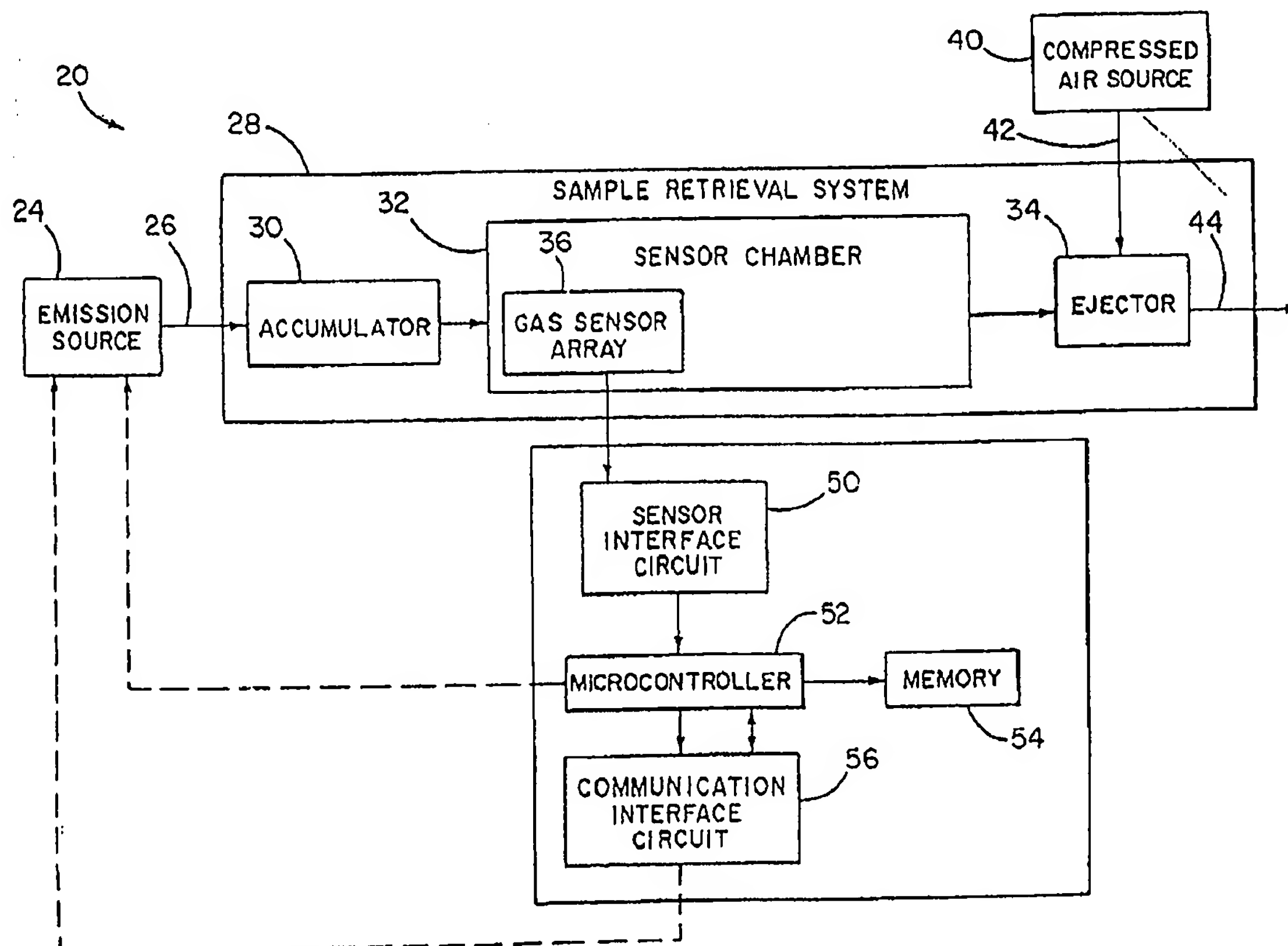
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(54) Title: CHEMICAL SENSOR WITH BLOCK COPOLYMER COATINGS



(57) Abrégé/Abstract:

Block copolymer or graft copolymer coatings and blends of block copolymers or graft copolymers with homopolymers and resins are used as a chemical absorption layer on a high performance, mass-sensitive, acoustic wave-based sensing device. The use of block copolymer coating materials containing polymer blocks with high and low glass transition temperatures within the same



(57) Abrégé(suite)/Abstract(continued):

molecule allows for tailoring of the absorption and physical characteristics of the absorptive layer on a sensor. The coatings form a composition that exhibits the necessary physical properties for use as the absorptive coating in an acoustic wave-sensing device. These materials have favorable acoustic properties over extended temperature ranges, resulting in a wider operating temperature range for acoustic wave-based sensing of volatile organic compounds. Moreover, the improved acoustic properties enable thicker coatings to be used, which increases the detection sensitivity of the sensor.

ABSTRACT OF THE DISCLOSURE

Block copolymer or graft copolymer coatings and blends of block copolymers or graft copolymers with homopolymers and resins are used as a chemical absorption layer on a high performance, mass-sensitive, acoustic wave-based sensing device. The use of block
5 copolymer coating materials containing polymer blocks with high and low glass transition temperatures within the same molecule allows for tailoring of the absorption and physical characteristics of the absorptive layer on a sensor. The coatings form a composition that exhibits the necessary physical properties for use as the absorptive coating in an acoustic wave-sensing device. These materials have favorable acoustic properties over extended
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CHEMICAL SENSOR WITH BLOCK COPOLYMER COATINGS**BACKGROUND OF THE INVENTION****1. Field of the Invention**

5 The present invention generally relates to systems for monitoring environmental contaminants and, more particularly, to systems in which acoustic wave-based chemical sensors are provided with absorbent coatings for monitoring fugitive emissions from process equipment.

10 **2. Background of the Invention**

Industrial plants that handle volatile organic compounds (VOCs) typically experience unwanted emissions of such VOCs and other volatilized compounds into the atmosphere from point sources, such as smoke stacks, and non-point sources, such as valves, pumps, and fittings installed in pipes and vessels containing the VOCs. Such VOCs may include, but are
15 not limited to, aromatics (e.g., benzene, toluene, ethylbenzene, and xylenes), halogenated hydrocarbons (e.g., carbon tetrachloride, 1,1,1-trichloroethane, and trichloroethylene), ketones (e.g., acetone, and methyl ethyl ketone), alcohols (e.g., methanol, ethanol, and propanol), ethers (e.g., dimethyl ether and methyl t-butyl ether), and aliphatic hydrocarbons (e.g., natural gas and gasoline). Inorganic compounds may also be carried into the
20 atmosphere along with or separately from the organic materials.

Emissions from non-point sources, referred to as fugitive emissions, typically occur due to leakage of the VOCs from joints and seals. Fugitive emissions from control valves may occur as the result of leakage through the packing between various parts of the valve,
25 such as between the valve stem and the body or bonnet of the valve or from damaged or worn areas within the transport system for the VOCs. Valves employed under demanding service conditions involving frequent movement of the valve stem, intense vibration, and large temperature fluctuations typically suffer accelerated deterioration of the valve stem packing, which results in statistically higher levels of fugitive emissions than valves employed in less
30 demanding service.

While improvements in valve stem packing materials and designs have reduced fugitive emissions and lengthened the life of valve packing, the monitoring of fugitive emissions has become important as a means of identifying and reducing fugitive emissions, and facilitates the ability of the systems to comply with more stringent regulations of emissions. For example, the Environmental Protection Agency (EPA) has promulgated regulations for specifying the maximum permitted emission of certain hazardous air pollutants from control valves, and requires periodic surveys of emissions from control valves. Where particularly noxious or toxic materials are transported through the valves, there is almost no tolerance for any fugitive emission. It therefore becomes important to be able to monitor the presence of leaks of such materials in a cost effective manner. This monitoring must be rapid, inexpensive, and reproducible.

Current methods of monitoring fugitive emissions involve manual procedures using a portable organic vapor analyzer. This manual method is time consuming and expensive to perform, and it can also yield inaccurate results due to ineffective collection of the fugitive emissions from the equipment being monitored. If measurements are made on a valve exposed to air currents or wind, emissions from the valve may be dissipated before the analyzer can properly measure the concentration of the emissions. Also, if the analyzer is not carefully moved around the exterior of the valve to capture all the emissions from the valve, an inaccurate measurement may result. Manual measurement methods also require plant personnel to dedicate a significant amount of time to making the measurements, thereby distracting plant personnel from other duties.

Automated monitoring and detection of fugitive emissions can yield significant advantages over existing manual methods. Some EPA regulations require surveys of fugitive emissions at periodic intervals. The length of the survey interval may be monthly, quarterly, semi-annually, or annually, with the required surveys becoming less frequent if the facility operator can document a sufficiently low percentage of control valves exhibiting excessive leakage. Achieving a low percentage of leaking valves may therefore reduce the number of surveys required per year. In a large industrial facility, where the total number of survey

points can range from 50,000 to 200,000, a reduced number of surveys can result in large cost savings. By installing automated fugitive emission-sensing systems on valves subject to the most demanding service conditions, and thus, monitoring those valves most likely to develop leaks, compliance with the EPA regulations can be more readily achieved for the entire
5 facility.

However, employing chemical sensors in an industrial environment requires designing sensors that perform satisfactorily in the presence of high relative humidity across a broad temperature range. The sensors must be able to discriminate between the emissions of
10 interest and other environmental contaminants, while retaining sufficient sensitivity to detect low concentrations of the fugitive emissions. A provision also must be made to enable periodic calibration of the chemical sensors. The output signals from the fugitive emission sensing system must be suitable for input into plant monitoring and control systems typically found in process plants. This remote sensing permits simple and inexpensive integration of
15 the sensing system into existing plant process control systems.

The fugitive emission sensing system should be inexpensive to manufacture, provide local notification of monitoring results (e.g., within an internal facility network system), and use a power source that is readily available in a typical process plant in order to keep
20 installation costs to a minimum. The system should be suitable for use in hazardous areas subject to risk of explosion, requiring electrical equipment to be intrinsically safe and/or of an explosion-proof design. The system also should be able to operate in harsh environments, including areas subject to spray washing, high humidity, high and low temperatures, and vibration. The system also should be simple and reliable, to keep maintenance costs to a
25 minimum.

In certain applications, the sensors used to detect fugitive emissions are provided in the form of piezoelectric-based sensors having high sensitivities to surface mass changes, so that when an alternating potential is applied across the sensors, changes in resulting acoustic
30 wave characteristics in the sensors, specifically the resonant frequency, indicate the presence

of the analyte, for example, the absorbed or adsorbed VOC. More specifically, the sensors typically include a quartz crystal substrate with conductive electrodes and an outer layer (on the electrodes) made of a material selected to most effectively absorb the analyte. Such outer coatings are selected to increase sensitivity, while reducing acoustic wave damping effects.

5 In addition, such materials should be environmentally robust to accommodate the aforementioned wide temperature ranges, humidity ranges, and high levels of dust particles and other contaminants.

Various Patent literature discusses the structure of such chemical sensors and the
10 compositions of the absorbing layers. U.S. Patent No. 5,883,457 describes the use of organic polymeric matrices as the coatings and particularly thermoset resins that are stable against ambient conditions.

U.S. Patent No. 5,900,128 describes the use of a protective intermediate layer
15 between the absorbing layer and an electrolyte precious metal layer.

U.S. Patent No. 5,910,286 describes the use of macroporous crosslinked layers with steric and functional configurations specifically suited to capturing molecular and/or ionic species.

20

The prior art, including the following U.S. Patents describe various structures and associated aspects of chemical sensors, some particularly quartz sensor, provides significant background on such chemical sensors. These patents include U.S. Patent Nos. 5,852,229; 5,936,150; 5,606,633; and 5,482,678.

25

SUMMARY OF THE INVENTION

An acoustic wave-based sensor according to the present invention is provided which may include at least one substrate, at least two electrodes connected to the at least one substrate, and a layer comprising a block or graft copolymer of at least two distinct polymer units having differing viscoelastic characteristics. The block or graft copolymers may be constituted of any combination of blocks or units of polymers that can be grafted or combined into polymeric combinations of film forming polymeric material. At least one unit of the at least two distinct units in the polymer must be capable of absorbing at least one volatile organic compound, and preferably two of the polymer units or all of the polymer units are capable of absorbing one or more volatile organic compound(s). The combination of distinct polymer units having differing viscoelastic properties (e.g., high and low glass transition temperatures (T_g)) within the same molecule facilitates tailoring of the acoustic properties of the polymeric film materials. These materials have favorable acoustic properties over extended temperature ranges, resulting in a wider operating temperature range for acoustic wave-based sensing of VOCs. Moreover, the improved acoustic properties enable thicker coatings to be used, which increases the detection sensitivity of the sensor. The combination of distinct polymer units also facilitates tailoring of physical absorption characteristics. That is, the distinct polymer units can be designed for sensitivity towards specific different VOCs so that a single sensor may be used to sense for two or more distinct volatile organic compounds. These block and graft copolymers may be blended or mixed into combinations with other physically compatible additives, including polymers and resins.

A method of detecting volatile organic compounds using the sensor of the present invention is provided. The sensor comprises a substrate, at least two electrodes connected to the substrate, and a coating positioned over the substrate and at least one of the electrodes. The coating is a block or graft polymer or polymeric mixture comprising at least two polymeric units, at least one unit being capable of absorbing at least one volatile organic compound.

These and other aspects and features of the present invention will become more apparent from the following detailed description when taken in conjunction with the accompanying drawings and examples.

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BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a block diagram of an illustrative fugitive emissions sensing system employing the chemical sensor of the invention.

Figure 2 shows a chemical sensor connected to an oscillator circuit for monitoring emissions.

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Figure 3 is a plot that compares sensitivity at 50 °C of quartz crystal microbalance (QCM) sensors coated with various polymeric films. The sensitivity to toluene, a representative VOC, in Hertz frequency change per ppm of toluene, is shown as a function of the resistance of the sensor. The varying resistance of the sensor is a result of the different thicknesses of the coatings.

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Figure 4 is a plot that compares the effect of temperature on the resistance of a sensor with a representative block copolymer-based coating vs. a homopolymer coating.

Figure 5 is a plot that compares the frequency response of a QCM coated with a representative block copolymer-based coating vs. a homopolymer coating at 50 °C. Resonant frequency change is plotted as a function of the gas phase concentration of the representative VOC toluene.

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Figure 6 is a plot that compares the speed of sensor response of a representative block copolymer-based coating vs. a homopolymer coating at -10 °C. The responses of each sensor have been scaled to the maximum response to 1000 ppm toluene in 15 minutes to facilitate comparison.

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DETAILED DESCRIPTION OF THE INVENTION

A sensor is provided which may include at least a substrate, at least two electrodes connected to the substrate, and a layer of a block or graft copolymer having at least a first polymeric unit and a second polymeric unit with differing viscoelastic properties (such as

differing T_g s), wherein at least one of the first and second polymeric units absorb at least one volatile organic compound.

One aspect of the present invention includes a chemical sensor comprising: a

5 substrate; at least two electrodes connected to the substrate; and a layer of polymer positioned over the substrate and at least one of the electrodes, wherein the layer of polymer comprises a polymeric layer selected from the group consisting of block copolymers, graft copolymers, and star copolymers. The block copolymer may preferably comprise at least 20% by weight of a block copolymer having at least two different blocks or a graft copolymer having at least

10 two different graft units, and the star copolymer contains at least two different monomer derived units, wherein different blocks or units within the block copolymer, graft copolymer or star copolymer have at least one property selected from the group consisting of volatile organic compound absorption characteristics, film strength and film brittleness different from the same property of at least one other block, star or graft unit in the layer. For example, the

15 block copolymer may comprise at least some units of a polymer derived from monomers having at least one ethylenically unsaturated polymerizable group. In particular, it is one embodiment to use a graft copolymer that comprises at least some units of a polymer derived from monomers having at least one ethylenically unsaturated polymerizable group, such as polymers with at least one monomer selected from the group consisting of olefins, styrenes,

20 butadienes, and vinyl resins. This invention enables the use of a layer of polymer with a thickness of between 1 and 10 micrometers. An example of the class of block copolymers comprises a block copolymer comprising AB diblock copolymer, ABA triblock copolymer, ABC triblock copolymer, and $(AB)_n$ copolymer. The chemical sensor may have the block copolymer comprise a combination of high T_g (e.g., above 40°C, above 50 °C, above 60°C, and above 70°C or 100 °C or more) and low T_g (e.g., less than 25°C, less than 20°C, less than

25 15°C, less than 10°C or less than 0 °C) polymeric blocks, preferably with a difference of at least 25°C between the high and the low T_g polymeric blocks. These types of chemical sensors using the block, graft or star copolymer coating may provide a rapid response time of less than 3 minutes for 90% response at -10 °C. The coatings may also provide the chemical

30 sensor with thermally stable response characteristics within the range of temperatures from

less than -10 °C to greater than 50 °C. The chemical sensor may be manufactured where the polymer layer was formed by spin coating. The chemical sensor may comprise a mass-sensitive acoustic wave chemical sensor or a sensor comprising a sensor selected from the group consisting of quartz crystal microbalances, surface acoustic wave devices, flexural mode sensors, optical sensors, electrochemical sensors and non-acoustic wave sensors.

The block copolymers may, for example, comprise elastomeric materials such as those known to those skilled in the art as A-B, A-B-A, A-B-C, or (A-B)_n block copolymers. These block copolymers are described, for example, in U.S. Pat. Nos. 3,265,765; 3,562,356; 3,700,633; 4,116,917 and 4,156,673, the substance of which is incorporated herein by reference. The block copolymers preferably comprise at least one polymeric unit derived from an ethylenically unsaturated monomer. Non-limiting examples of such block copolymers comprise styrene, isoprene, butadiene, ethylene-styrene, halogenated poly(vinyl aromatics), and/or butylenes based (SIS, SBS or SEBS) block copolymers, acrylate (including methacrylate) block copolymers, urethane block copolymers, silicone resin block copolymers, and mixed resin system block copolymers. Other useful elastomeric compositions can include elastomeric block copolymers of polyurethanes, polyamides, poly(N,N-dialkylacrylamides), poly(vinylpyridines), ethylene copolymers such as ethylene vinyl acetates, ethylene/propylene copolymer elastomers or ethylene/propylene/diene terpolymer elastomers. Blends of these elastomers with each other or with modifying non-elastomers are also contemplated. The properties of block copolymers can be tailored by incorporating additives that preferentially associate with one of the polymeric units. With regard to acoustic properties, the effect of the additive depends on whether the additive has a higher or lower softening point than the associated polymeric unit. For example, additives that associate with a high T_g unit and have a lower T_g will lower the softening point of that unit. Conversely, an additive with a higher softening point will raise the softening point of the unit. For example, up to 50 weight percent, but preferably less than 30 weight percent, of polymers can be added as stiffening aids, such as polyvinylstyrenes, polystyrenes such as poly(alpha-methyl)styrene, polyesters, epoxies, polyolefins, e.g., polyethylene or certain ethylene/vinyl acetates, preferably those of higher molecular weight, or coumarone-indene

resin. The ability to use these types of elastomers and blends provides the invention film material with significant flexibility in tailoring the absorption and acoustic properties of the film.

5 As noted, acrylic (including methacrylic) polymers, conjugated or not conjugated block copolymers, including diene polymer blocks, such as a polymer block comprising an olefinic monomer and a polymer block comprising at least one constitutional unit selected from the group consisting of an acrylic, methacrylic, (meth)acrylic acid, (meth)acrylate and (meth)acrylonitriles such as those selected from the group consisting of acrylic acid,
 10 methacrylic acid, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, dodecyl acrylate, 2-hydroxy ethyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, dodecyl methacrylate, 2-hydroxy ethyl methacrylate, glycidyl acrylate, glycidyl methacrylate, dimethylaminoethyl acrylate and quaternary salts thereof, dimethylaminoethyl methacrylate and quaternary salts
 15 thereof, acrylonitrile, and methacrylonitrile, and mixtures thereof. Hydrogenated or non-hydrogenated derivatives may be used. An example of a thermoplastic polymer composition of this class might have a degree of hydrogenation of the hydrogenated conjugated diene polymer block (B) not smaller than 50 mol%. Typically, the average molecular weight (number average value M_n) of each block or graft unit present is within the range from 3000
 20 to 500,000, preferably from 10,000 to 200,000 g/mol.

Viscosity reducing polymers and plasticizers can also be blended with the elastomers such as low molecular weight polyethylene and polypropylene polymers and copolymers, or tackifying resins such as Wingtack®, aliphatic hydrocarbon tackifiers available from
 25 Goodyear Chemical Company. Tackifiers can also be used to increase the adhesiveness of an elastomeric core(s) to the matrix material. Examples of tackifiers include aliphatic or aromatic liquid tackifiers, aliphatic hydrocarbon resins, polyterpene resin tackifiers, and hydrogenated tackifying resins. Aliphatic hydrocarbon resins are preferred. Additives such as dyes, pigments, antioxidants, antistatic agents, bonding aids, antiblocking agents, slip
 30 agents, heat stabilizers, photostabilizers, foaming agents, glass bubbles, starch and metal salts

for degradability or microfibers can also be used in the elastomeric core layer(s). Suitable antistatic aids include ethoxylated amines or quaternary amines such as those described, for example, in U.S. Pat. No. 4,386,125 (Shiraki), who also describes suitable antiblocking agents, slip agents and lubricants. Softening agents, tackifiers or lubricants are described, for example, in U.S. Pat. No. 4,813,947 (Korpman) and include coumarone-indene resins, terpene resins, hydrocarbon resins and the like. These agents can also function as viscosity reducing aids. Conventional heat stabilizers include organic phosphates, trihydroxy butyrophene or zinc salts of alkyl dithiocarbonate. Oxidation is an important issue when the acoustic wave sensing devices are placed in the presence of strong oxidizing compounds such as ozone, sometimes found in industrial environments. Suitable antioxidants include hindered phenolic compounds and amines possibly, with thiodipropionic acid or aromatic phosphates or tertiary butyl cresol, see also U.S. Pat. No. 4,476,180 (Wnuk) for suitable additives and percentages. The use of chemical additives should be minimized to maintain a high level of absorbency, so that plasticizers and chemical additives in addition to the block copolymer itself should be maintained below 2%, preferably below 1.5%, below 1%, below 0.5%, below 0.1%, for example.

Graft copolymers may also be used, including those prepared by such diverse methods as shown in U.S. Patent No. 6,114,460; 6,114,440; 6,107,440; 6,100,331; 6,096,827; 6,060,566; 6,054,539; and the like. The graft or block copolymers are used in essentially identical manners after being prepared, being coated onto the surface of the sensor, using such coating methods that provide an appropriately uniform coating, for example, dip coating, spray coating, evaporative coating methods, sputter coating, spin coating and the like.

25

Short fibers or microfibers can be used to reinforce the block or graft copolymer for certain applications. These fibers are well known and include polymeric fibers, mineral wool, glass fibers, carbon fibers, silicate fibers and the like. Further, certain particles can be used, including carbon and pigments.

30

Glass bubbles or foaming agents are used to lower the density of the elastomeric layer and can be used to reduce cost by decreasing the elastomer content. These agents can also be used to increase the bulk of the elastomer. Suitable glass bubbles are described in U.S. Pat. Nos. 4,767,726 and 3,365,315. Foaming agents used to generate bubbles in the elastomer
5 include azodicarbonamides. Fillers can also be used to some extent to reduce costs. Fillers, which can also function as antiblocking agents, include titanium dioxide and calcium carbonate.

According to the present invention, a polymer layer comprising a mixture of at least
10 one block or graft copolymer (hereafter referred to as a "polymeric mixture") is positioned over the substrate and at least one of the electrodes of the sensor. The polymer may comprise any form of mixture of the block or graft copolymer and additives (whether a mixture, blend, solid state solution, suspension, dispersion, interpenetrating network or the like), alone or in admixture with other physically compatible polymers. The polymeric mixture should be able
15 to absorb (or less preferably adsorb) volatile organic compounds onto its surface or into pores within its macro-structure or molecular structure. An increase in the total mass of the coating on the sensor from absorption of the VOCs causes a change (typically a decrease) in the resonant frequency of the sensor according to conventional mathematic and physics principles relating to the effect of mass increases on resonant frequencies. This change in
20 resonant frequency provides a detectable signal to the sensing device that VOCs are present. Both the pore size of the blended coating, additives provided within the polymer (including polymeric plasticizers or solid additives with specific absorption characteristics), its surface energy, oleophilicity/hydrophilicity, oleophobicity/hydrophobicity, and even active groups in the polymer may be altered to tailor the absorption of the unit to more specific VOCs or to
25 keep the absorption of VOCs more general.

Referring now to the drawings, and with specific reference to Fig. 1, a fugitive emissions sensing system utilizing the present invention is generally depicted by reference numeral 20. However, it is to be understood that the present invention is primarily directed to a chemical sensor 22 (Fig. 2) which can be employed in a variety of applications, including applications separate from the fugitive emissions sensing system 20.

By way of overview, Figure 1 is a block diagram of an illustrative fugitive emissions sensing system 20 employing the chemical sensor 22. An emission source 24 is shown, from which a sample stream 26 is drawn into sample retrieval system 28. The sample retrieval system 28 includes an accumulator 30, a sensor chamber 32, and an ejector 34. A chemical sensor array 36 is located within the sensor chamber 32. The sample stream 26 is drawn from the accumulator 30 into the sensor chamber 32, exposing the chemical sensor array 36 to the sample stream 26. The chemical sensor array 36 contains one or more of the chemical sensors 22. The sample stream 26 then passes into the ejector 34. A compressed air source 40 provides compressed air 42 to the ejector 34, creating a pressure drop within the ejector 34 that draws a sample stream 26 through the sensor chamber 32 and into the ejector 34. The compressed air 42 and sample stream 26 are mixed within the ejector 34 and exhausted to atmosphere as a mixture 44.

The gas sensor array 36 is connected to a sensor interface circuit 50, which processes the signals from the sensor array 36 and provides the process signals to a microcontroller 52. The microcontroller 52 stores the data from the sensors 22 in a memory 54, and uses the sensor data received from the fugitive emissions sensing system 20 to initiate control actions to reduce or eliminate the emissions. For example, the microcontroller 52 could close a valve upstream from the emissions source 24 to stop the flow of fluid through the emissions source 24 in order to stop emissions caused by the leakage of the fluid. Alternatively, the microcontroller 52 could alter operating conditions of the emissions source 24 to reduce or eliminate the fugitive emissions. The microcontroller 52 may use a communication interface circuit 56 to provide control signals to the upstream valve, the emission source 24, or any other equivalent that may be used to reduce or eliminate the emissions. The microcontroller

52 may also be able to provide signals to distal locations to provide warnings or signals. Such distal locations could include firefighting locations (which are often responsible for addressing chemical leaks) or other safety or emergency facilities.

5 It can therefore be seen that the fugitive emissions sensing system 20 may be used to detect the presence of, or measure the concentration of, various types of fluids emitted from the emissions source 24, and to provide controls and signals relating to the status of the concentrations of the fluids monitored emissions. The system may be used to detect hazardous, toxic or polluting substances emitted from the source, or to detect leakage of
10 non-hazardous substances, the loss of which may be a cause of concern. The fugitive emission sensing system 20 may be used to detect emissions from any kind of source, particularly industrial process equipment or hospital equipment from which hazardous substances may leak. Examples include control valves, block valves, pumps installed on lines carrying hazardous gases, sterilizers, agitators, screw conveyors, or other equipment
15 installed on process vessels containing hazardous fluids, hazardous materials that are being treated, heat exchanges, reactors, etc. When emissions are detected by the fugitive emissions sensing system 20, this data may be used by the fugitive emissions sensing system 20 to control the process in such a way as to reduce or eliminate the emissions.

20 As indicated above, the chemical sensor array 36 may include one or more chemical sensors 22 responsive to a particular analyte or fugitive emission being monitored. In the embodiment depicted in Figure 2, the chemical sensor 22 is a quartz crystal microbalance (QCM) sensor, but can be another type of piezoelectric acoustic wave devices, including surface acoustic wave (SAW) devices, acoustic plate mode (APM) devices, and flexural plate
25 wave (FPW) devices. Alternatively, fiber optic sensors and electrochemical sensors may be used.

As shown in Figure 2, the chemical sensor 22 may be connected to an oscillator circuit 62 for monitoring emissions. In an alternative embodiment, the chemical sensor 22
30 could be connected to a network analyzer. More specifically, the oscillator circuit 62 may

include NAND gates 64 and 66, and an AND gate 68, connected in series. A resistor 70 may be connected between the output of the NAND gate 66 and the circuit power supply voltage 72, and a resistor 74 may be connected between the output of NAND gate 66 and circuit power supply voltage 72. A resistor 75 may be connected across the NAND gate 64, connecting a first input to the output. A select signal 76 may be connected to the second input of the NAND gate 64, and the same select signals may also be connected to an input of the AND gate 68. An enable signal 78 may be connected to an input of the NAND gate 66. When the select signal 76 and the enable signal 78 are both high, the NAND gates 64 and 66 act as high-gain inverting amplifiers and cause an oscillator 80 to oscillate between high and low voltage, producing an oscillating square wave output. The oscillating voltage from the oscillator output 80 may be transferred through the AND gate 68 and applied across the chemical sensor 22 causing the chemical sensor 22 to physically resonate.

In order to appreciate the significance of this resonance, it is first important to understand that the chemical sensor 22 utilizes the converse piezoelectric effect. By way of background, the piezoelectric effect holds that a mechanical stress applied to the surfaces of various crystals, including quartz, affords a corresponding electrical potential across the crystal having a magnitude proportional to the applied stress. The electrical charge generated in the quartz crystal under stress is due to the shift of dipoles resulting from the displacement of atoms in the crystalline material. The converse piezoelectric effect holds that application of a voltage across certain crystals, including quartz crystals, results in a corresponding mechanical strain in the crystal. In quartz, this strain or deformation is elastic. It follows that an alternating potential across the crystal causes a vibrational or vibratory motion in the quartz crystal, i.e., the aforementioned resonance. The chemical sensor 22 therefore includes a crystal substrate 82 which interacts with the oscillating circuit 62, and in turn causes the oscillator circuit 62 to oscillate at the resonant frequency of the chemical sensor 22. Thus, the frequency of the oscillator output 80 will vary as the resonant frequency of the chemical sensor 22 varies, and the resonant frequency of the chemical sensor varies in proportion to the amount of absorbed material, the absorbed material at least increasing the mass on the vibratory surface or vibratory elements of the chemical sensor 22 device.

The resonant frequency of the chemical sensor 22 can vary based on a number of parameters, including the mass, size, shape, and cut of the substrate 82. That substrate is preferably a crystalline substrate, such as a quartz crystal substrate 82. Quartz crystal exhibits a natural resonant frequency that is a function of the mass and structure of the crystal. The precise size, type of cut, and thickness of the quartz crystal substrate 82 are selected to result in a particular resonant frequency. For example, an AT-cut crystal with a nominal resonant frequency of 8-30 megahertz is suitable for gas sensor applications. Suitable quartz crystal substrates may be obtained from Standard Crystal Corporation of California. Other types of suitable materials to serve as the substrate include lithium niobate (LiNbO_3), which is particularly suited for a surface acoustic wave (SAW) based-sensor; and aluminum nitride (AlN), which is particularly suited for a thin film resonator based-sensor.

In order to apply the alternating potential across the substrate 82, first and second electrodes 84 and 86 are connected to the crystal substrate 82 and may be constructed of gold-on-chromium, although other suitable corrosion-resistant conductors may be used, possibly including aluminum, palladium, gold, chromium, and graphite. The electrodes 84 and 86 may serve as both the conductors for generating the alternating current across the crystal substrate 82, and as transducers for sensing parameters related to changes in resonant frequencies resulting in the crystal substrate 82.

As indicated above, the resonant frequency of the chemical sensor 22 is primarily a function of the total mass of the device (although alterations in flexibility or stiffness of the coating because of the effects of absorbents or temperature changes may also similarly influence the resonant frequency). Therefore, the mass of any coating provided around the crystal substrate 82 also affects the total mass of the device, and thereby affects the resonant frequency of the chemical sensor 22. The coatings provided about the crystal substrate 82 are selected to absorb molecules of the analyte. When analyte molecules are absorbed by the coating, the mass of the coating is slightly increased, which in turn increases the mass of the entire sensor 22, and thus changes the resonant frequency of the sensor 22. The resonant

frequency of the chemical sensor 22 is also a function of the viscoelastic properties of the coatings and mechanical stresses caused by temperature effects in the sensor mounting structure. However, viscoelastic effects are reduced for coatings as in this invention and mechanical stress effects are either negligible or can be compensated for. Thus, a very
5 sensitive chemical detector may be constructed by selecting a coating that has a chemical affinity for the particular analyte of interest. The quantity of molecules absorbed and deposited, and the resulting change in the operating frequency of the oscillator circuit 62, is a function of the concentration of the analyte being measured in the environment surrounding the chemical sensor 22. The frequency changes linearly with changes in analyte
10 concentration, within certain limits.

Thus, a change in the concentration of the analyte may be measured by measuring the change in the frequency of the oscillator output 80. The chemical sensor 22 may be calibrated by exposing the chemical sensor 22 to known concentrations of the analyte and
15 recording the resulting frequency of the oscillator output 80. The chemical sensor 22 may then be used to measure the absolute concentration of the analyte by comparing the measured frequency to the aforementioned recorded values.

The particular coating chosen for the crystal substrate 82 should preferably readily
20 absorb the molecules of the analyte, to provide fast response times and a high degree of sensitivity to the analyte over a broad temperature range, but do so without damping the generated waves. Additionally, the coating should not degrade by oxidation. The present invention provides such a coating in the form of a graft or block copolymer coating 88.

25 Mass-sensitive acoustic chemical sensors, such as polymer-coated QCMs and surface acoustic wave (SAW) devices, are used for the detection and monitoring of VOCs (J.W. Grate, S.J. Martin and R.M. White, *Anal. Chem*, 1993, 65, pp. 957A-996A). Ideally, the sensitivity of such sensors is directly proportional to the thickness of the polymeric coating. Coating development to date has focused primarily on polymers with glass transition
30 temperature (usually the first order glass transition temperature, but the second order glass

transition temperature may also be considered), T_g below room temperature because vapor sorption in soft rubbery polymers is rapid and reversible. Such polymers, however, are not optimal for use in acoustic wave-based devices because they have a low shear modulus, and therefore poor acoustic wave properties (Kanazawa, K.K., *IBM Research Report, Physics*, 5 1986, RJ 5125, 53236). As a result of these deficiencies in properties, the usable film thickness, and hence sensitivity, of soft polymers is limited by the attenuation of the acoustic energy. The operating temperature of the device also affects the upper limit of the thickness. As the temperature increases, the shear modulus of the film decreases, resulting in further damping of the acoustic wave (J.W. Grate, *supra*). Stiff, high T_g polymers have a higher 10 shear modulus, but exhibit slow VOC uptake and release. Using very thin films can reduce the uptake and release times. At the same time, unfortunately, this results in reduced detection sensitivities.

It was found that coatings made from blends of low and high T_g polymers (U.S. Patent 15 Application, U.S. Serial No. 09/413,401, in the names of R. Shinar et al.) can be used at relatively large thicknesses in acoustic-wave based chemical sensors without significantly damping the acoustic wave. Such coatings have the advantage of combining the preferred properties of soft and stiff polymers, thereby creating fast-responding, highly sensitive coatings with improved acoustic properties, and therefore enhanced performance at elevated 20 temperatures (Shinar et al., *supra*). Alternatively, the component polymers can be linked together into a single polymer chain, effectively 'chemically blending' the polymers and hence avoiding issues of macroscopic phase separation. Polymers in which large segments are composed of one type of polymer, followed by a segment of a different polymer, are called block copolymers. This invention describes the use of block and graft copolymers to 25 produce acoustic wave-based sensors of improved performance.

The unique physical properties of thermoplastic elastomer block copolymers arise because the blocks that make up the polymer molecules are chemically incompatible. Because of this incompatibility, there is a thermodynamic driving force toward phase 30 separation. The similar blocks from different polymer chains associate strongly with one

another. However, macroscopic phase separation is prevented by the chemical bonding between incompatible blocks in individual polymer chains. The result is the generation of microphase domains. These domains are physically, rather than chemically crosslinked. Since the material is not chemically crosslinked, it can be melted and dissolved, facilitating thin film coating fabrication. The physical properties of block copolymers are a combination of the properties of the component blocks. We have found that the 'chemical blending' of high T_g and low T_g polymers into a single polymer chain, and the physical crosslinking of these chains, results in coatings with favorable acoustic properties for acoustic wave-based chemical sensors.

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We observed also that f and R values of block and graft copolymer coatings of component ratios of between 1%-99% and 99% to 1% for two block systems were useful, although performance would appear to tend towards a distinctly averaging level. That is, if blocks A and Blocks B were combined in 50/50 proportions, the performance of the system would be the performance expected by averaging the performance characteristics of pure 100% A polymer and 100% B polymer. It is preferred to obtain a measurable effect of the combination of the two blocks (as a 1% level would provide minimum or even unmeasurable benefit in excess of the accuracy of the measurements from the 1% component), and this would be accomplished by using proportions in two component system of between 5-95%A/95%-5%B, 10-90%A/90-10%B, 15-85%A/85%-15%B, 20-80%A/80-20%B, 25-75%A/75-25%B, 30-70%A/70-30%B, 35-65%A/65-35%B, 40-60%A/60-40%B, 45-55%A/55-45%B, and 50/50 block or graft ratios.

The polymer units in the graft or block copolymers may be selected on the basis that each of the units may have similar physical/chemical absorption properties and different physical structural properties so that a good balance may be achieved in the physical structural properties while maintaining the appropriate absorption properties. Similarly, each polymer unit may have good physical structural properties, but differ too extremely in their absorption characteristics towards a specific VOC or towards a group of distinct VOCs. For example, although A and B may have good VOC absorption properties, a polymer from only

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A blocks might be too brittle, and a polymer from only B blocks may be too soft. By forming a graft or block copolymer from the two distinct units, the good VOC absorption properties may be maintained, but an acceptable intermediate structural physical property attained. Block A may have good VOC absorption properties towards a highly non-polar organic and B might have good VOC absorption towards a highly polar VOC. To have a sensor that is capable of responding to both types of VOCs, it would therefore be desirable to have both A units and B units available in the polymer coating on the sensor.

The coatings according to the present invention exhibited favorable attributes observed in blends of high and low T_g polymers. These included reduced damping of the acoustic wave, which enables sensor operation at elevated temperatures (R. Shinar et al., *supra*). Thick coatings (e.g., from 1 to 10 micrometers, 4-6.5 micrometers, especially ~5.5 μm) of the graft or block polymers or blends according to the present invention, with excellent performance characteristics (typical of high and low T_g polymer blends) over a wide temperature range of -10 to 50°C, can be used in sensor applications for long periods

While the invention is susceptible of various modifications and alternative constructions, certain illustrated embodiments have been shown in the drawings and will be described below in detail. It should be understood, however, that there is no intention to limit the invention to the specific form disclosed, but on the contrary, the intention is to cover all modifications, alternative constructions, and equivalents, falling within the spirit and scope of the invention as defined by the appended claims.

Example I

Experiments that demonstrate the advantages of using block copolymer films as sensor coatings were conducted using AT-cut quartz crystal microbalances (QCMs) as the acoustic wave-based sensor. Analogous results are expected using other acoustic wave-based sensor platforms (e.g., surface acoustic wave devices). The invention described here has been demonstrated using triblock copolymers having the two end blocks made from

polystyrene and a midblock containing a rubbery polymer component. Similar results can be expected using different block copolymer architectures. Table 1 lists the copolymers tested.

Table 1

Polymer
polystyrene- <i>block</i> -poly(ethylene- <i>ran</i> -butylene)- <i>block</i> -polystyrene ⁽¹⁾
polystyrene- <i>block</i> -polybutadiene- <i>block</i> -polystyrene
polystyrene- <i>block</i> -poly(ethylene- <i>ran</i> -butylene)- <i>block</i> -polystyrene blended with poly(2,6-dimethyl- <i>p</i> -phenylene oxide) ⁽²⁾
polystyrene- <i>block</i> -poly(ethylene- <i>ran</i> -butylene)- <i>block</i> -polystyrene blended with coumarone-indene resin ⁽³⁾
polystyrene- <i>block</i> -polybutadiene- <i>block</i> -polystyrene blended with coumarone-indene resin

⁽¹⁾ Kraton G1652 and Kraton G1654 from Shell Chemical

5 ⁽²⁾ Blend is Kraton G7723x from Shell Chemical

⁽³⁾ Resin is Cumar LX-509 from Neville Chemical

Polymer film coatings can be made by a number of techniques. Typically, the starting material is a solution of the block copolymer in an appropriate solvent. The solvent can either dissolve one of the blocks preferentially or be a good solvent for all blocks of the copolymer. The choice of solvent can impact the morphology of the films and thus potentially their acoustic properties. To date, all studies have been conducted using films made from solutions of block copolymers dissolved in toluene, which is a good solvent for all of the components of the block copolymers tested. Techniques for forming thin films of block copolymers on the acoustic wave sensor include spin coating, spray coating, and dip coating. We have tested coatings formed by spin coating, spray coating, and dip coating and have observed comparable results. The sensors were made by coating both sides of ~10 MHz QCMs with solutions that ranged between 5% and 12% w/v and allowing the solvent to evaporate. A network analyzer was used to measure the resonant frequency of the QCM as a function of analyte concentration and temperature. The network analyzer also measured the dissipation of energy in the QCM, in units of resistance (Ohms), which is related to the acoustic loss in the device. Other types of impedance analyzers can also be used for these measurements. Field-deployable sensors typically incorporate the QCM in an oscillator circuit and employ a frequency counter to measure the resonant frequency. These devices cannot sustain oscillation if the resistance is too high (i.e., if the acoustic loss is too high).

This occurs when $R > 1/(\omega_0 C_0)$ where R is the resistance, ω_0 is the angular resonant frequency of the quartz crystal and C_0 is the static capacitance of quartz. For typical QCMs, the maximum resistance is therefore 1-2 k Ω . We chose 100 Ω as a reference resistance level at which to compare sensor performance. Resistances of this magnitude usually do not prevent resonator oscillation.

Figure 3 shows the performance at 50 °C of coatings of ABA block copolymers and mixtures of block copolymers and additives compared to the homopolymers polyisobutylene (PIB) and poly(diphenoxyphosphazene) (PDPP). This figure displays the measured sensitivity of various coatings, defined as the change in oscillation frequency of the sensor per unit concentration of VOC, (parts per million toluene in this example), as a function of resistance. The sensitivity of a coating increases approximately linearly with coating thickness because the amount of VOC sorbed by the coating is proportional to the amount of coating on the sensor. Resistance is a measure of acoustic loss in the device, which usually increases with temperature. It also increases with thickness, but much more rapidly than sensitivity (roughly exponentially). The maximum sensitivity of a coating is thus limited by the maximum resistance (i.e., acoustic loss) that can be tolerated. Figure 3 displays sensor resistance and sensitivity data measured for coatings of various thickness. It is seen that the block copolymers outperform the homopolymers in terms higher sensitivity at a given level of resistance (see Table 2 for a comparison of sensitivities at a reference resistance of 100 Ω , interpolated or extrapolated from the data in Figure 3).

Table 2

Polymer	Sensitivity ⁽¹⁾ (Hz/ppm toluene)
Homopolymers	
PDPP	0.10
PIB	0.11
Block Copolymers and Blends	
SEBS ⁽²⁾	0.15
SBS	0.22
SEBS + PPO ⁽³⁾	0.24
SEBS + coumarone-indene resin ⁽⁴⁾	0.48

⁽¹⁾ Sensitivity to toluene at 50 °C at a thickness that gives a resistance of 100 Ω

⁽²⁾ Shell Kraton G1652

⁽³⁾ Shell Kraton G7723x

⁽⁴⁾ Shell Kraton G1652 + Neville Cumar LX-509

The SEBS polymers tested were Kraton G1652 and G1654x. Kraton G1654x has a styrene content of 31% and has a molecular weight approximately twice that of Kraton G1652, which has a styrene content of 30%. They dissolve readily in toluene, producing films with fast response times (2-3 minutes to reach 90% of full response at -10 °C, the lowest temperature tested) and linear calibration curves (correlation coefficients >0.99). There is very little difference between the two in term of sensor resistance and sensitivity.

The polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) tested had a styrene content of 28% and is a block copolymer with very good sensor characteristics. A 2.5 µm coating of SBS has a sensitivity comparable to a 4.9 µm PIB film, but has a faster response time at -10 °C (1 minute vs. 15 minutes to reach 90% of full response). The resistance of this sensor was ~100 Ω at 50 °C, compared to 320 Ω for the 4.9 µm PIB coating.

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Block Copolymers Blended with Additives to Enhance Performance

The commercially available blend Kraton G7723x contains roughly 20% poly(2,6-dimethyl-*p*-phenylene oxide), a high T_g polymer that is miscible with polystyrene, and 80% Kraton G1652, an SEBS triblock copolymer. The poly(2,6-dimethyl-*p*-phenylene oxide) makes Kraton G7723x stiffer than Kraton G1652. Because of its lower acoustic loss, it was possible to make thicker, and consequently more sensitive coatings with this material than with Kraton G1652.

High melting point resins can also associate with the polystyrene phase of these block copolymers and raise their softening point. An example is Cumar LX-509, a coumarone-indene resin manufactured by Neville Chemical Co. Tests were made with blends of SEBS and SBS block copolymers with this resin. The addition of Cumar LX-509 to the SEBS block copolymers enhanced their performance dramatically (Figure 3 and Table 2). The maximum sensitivity at 100 Ω is three times greater than that obtained without the.

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coumarone-indene resin. This improvement is due to the lower acoustic loss of this coating material, which permits thicker coatings to be used. Importantly, rapid response times at low temperature were maintained.

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Example II

The improvement in sensor performance is further illustrated in Figure 4. Figure 4 shows how the resistance, (i.e., acoustic loss) of sensors with representative coatings is affected by temperature changes. It is particularly noteworthy that the blend of Kraton G1652 with Cumar LX-509 shows a decrease in acoustic loss at elevated temperatures. This relatively stable acoustic loss permits the use of much thicker coatings of this material, which sorb more VOC, and operation of sensors coated with this material over the full temperature range of -10°C to 50°C .

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Example III

Figure 5 illustrates the enhanced sensitivity achievable with block copolymer coatings and the linearity of sensor response. For the particular coatings tested at 50°C , the sensitivity of the block copolymer coating was 0.77 Hz/ppm toluene with a correlation coefficient, r^2 , of 0.9997 . In comparison, the PIB coating sensitivity was much lower, 0.21 Hz/ppm with $r^2 = 0.9980$. The thickness of the block copolymer coating ($10\text{ }\mu\text{m}$) was chosen to maintain the resistance below $100\text{ }\Omega$. In contrast, the lower sensitivity of the PIB coating is in spite of a thickness ($4.9\text{ }\mu\text{m}$) that was too large to maintain this level of resistance. The resistance of the PIB-coated sensor was $320\text{ }\Omega$.

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Example IV

Figure 6 demonstrates that the sensor response time can be improved through the use of block copolymer coatings. Shown is a plot that compares the speed of sensor response of a representative block copolymer-based coating vs. a homopolymer coating at -10°C . The responses of each sensor have been scaled to the maximum response to 1000 ppm toluene in 15 minutes to facilitate comparison. It is seen that at -10°C , the block copolymer/resin coating responds more quickly than a PIB coating of $1/2$ the thickness.

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WHAT IS CLAIMED:

1. A chemical sensor comprising:

a substrate;

5 at least two electrodes connected to the substrate; and

a layer of polymer positioned over the substrate and at least one of the electrodes,

wherein the layer of polymer comprises a polymeric layer selected from the group consisting of block copolymer, graft copolymers, and star copolymers.

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2. The chemical sensor of claim 1 wherein the block copolymer comprises at least 20% by weight of a block copolymer having at least two different blocks or a graft copolymer having at least two different graft units, and the star copolymer contains at least two different monomer derived units, wherein different blocks or units within the block copolymer, graft copolymer or star copolymer have at least one property selected from the group consisting of volatile organic compound absorption characteristics, film strength and film brittleness different from the same property of at least one other block, star or graft unit in the layer.

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3. The chemical sensor of claim 1 wherein the polymer layer comprises a block copolymer.

4. The chemical sensor of claim 1 wherein the polymer layer comprises a graft copolymer.

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5. The chemical sensor of claim 3 wherein the block copolymer comprises at least some units of a polymer derived from monomers having at least one ethylenically unsaturated polymerizable group.

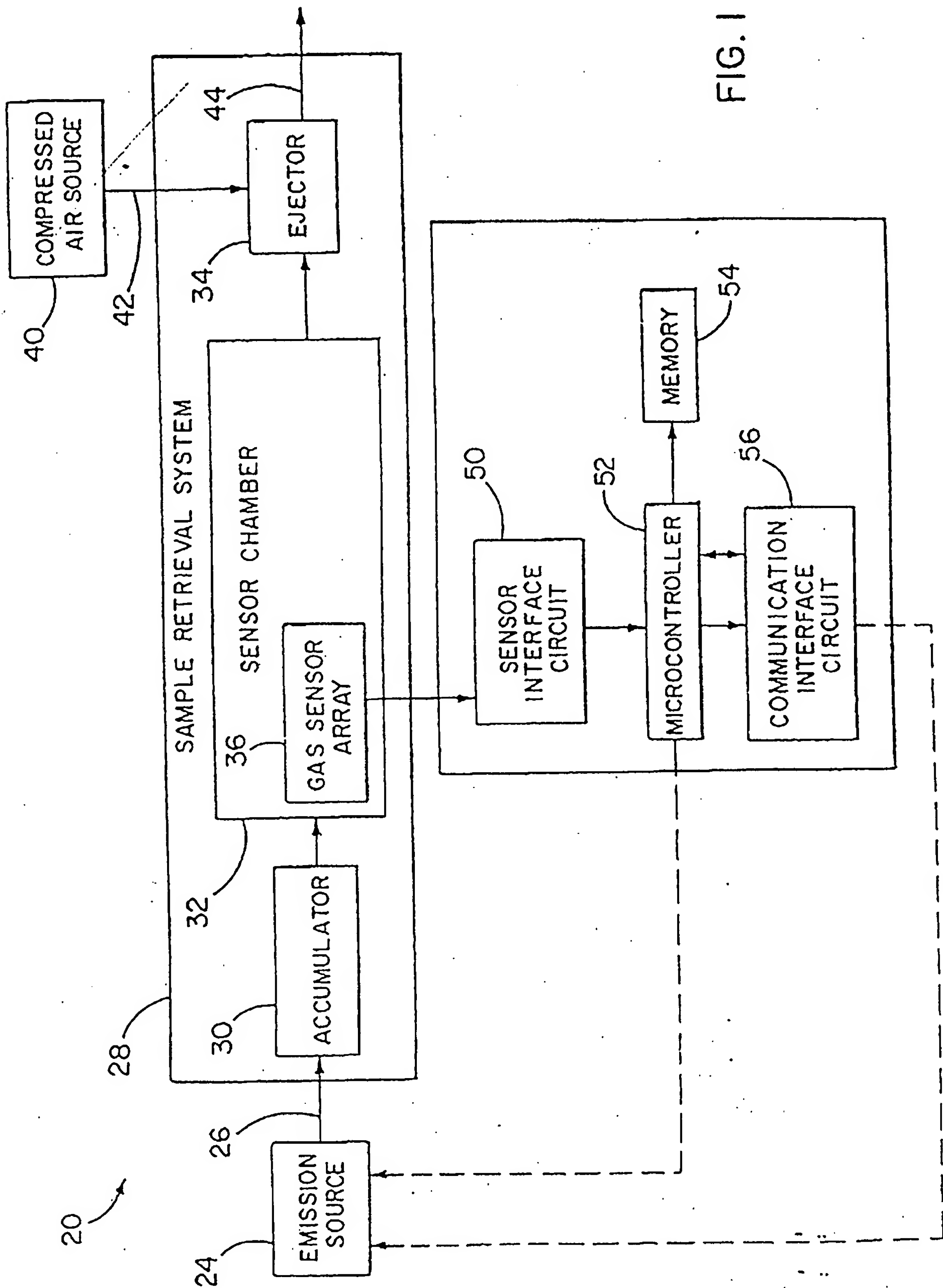
6. The chemical sensor of claim 4 wherein the graft copolymer comprises at least some units of a polymer derived from monomers having at least one ethylenically unsaturated polymerizable group.
- 5 7. The chemical sensor of claims 1, 2, 3, 4, 5, or 6 wherein the layer of polymer has a thickness of between 1 and 10 micrometers.
8. The chemical sensor of claim 7 wherein the layer of polymer comprises at least 10% by weight of polymeric units derived from at least one monomer selected from the group
10 consisting of olefins, styrenes, butadienes, and vinyl resins.
9. The chemical sensor of claim 3 wherein the block copolymer comprises a block copolymer comprising AB diblock copolymer, ABA triblock copolymer, ABC triblock copolymer, and $(AB)_n$ copolymer.
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10. The chemical sensor of claim 1 wherein the copolymer comprises a star copolymer.
11. The chemical sensor of claim 3 wherein the block copolymer comprises a combination of high Tg and low Tg polymeric blocks with a difference of at least
20 25°C between the high and the low Tg polymeric blocks.
12. The chemical sensor of claim 3 wherein the block copolymer coating has a rapid response time of less than 3 minutes for 90% response at -10°C .
- 25 13. The chemical sensor of claim 3 wherein the sensor shows thermally stable acoustic response characteristics within the range of temperatures from less than -10°C to greater than 50°C .
- 30 14. The chemical sensor of claims 1, 2, 3, 4, 5, or 6 comprising a mass-sensitive acoustic wave chemical sensor.

15. The chemical sensor of claim 3 wherein the sensor comprises a sensor selected from the group consisting of quartz crystal microbalances, surface acoustic wave devices, flexural mode sensors, optical sensors, electrochemical sensors and non-acoustic wave sensors.

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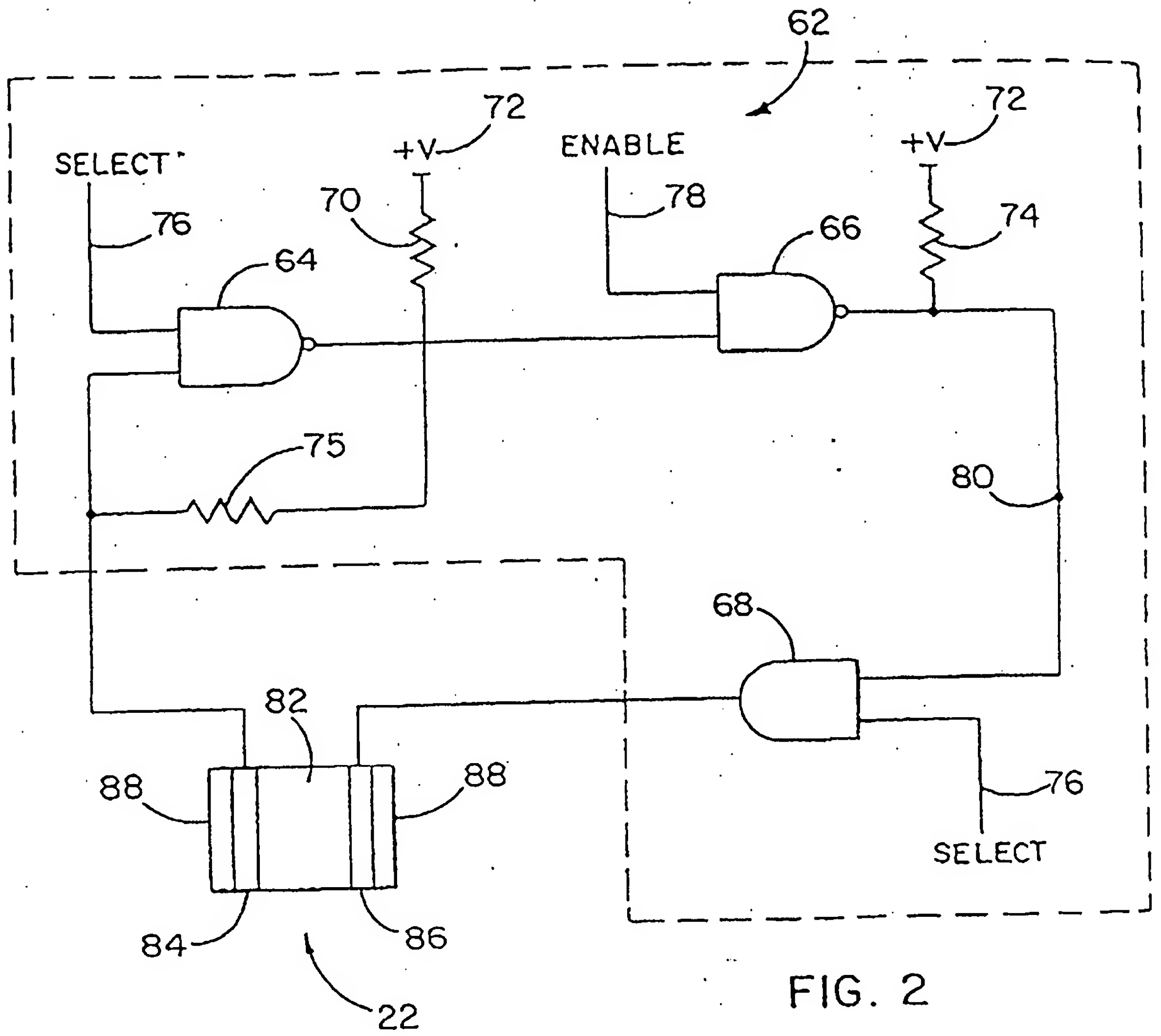


FIG. 2

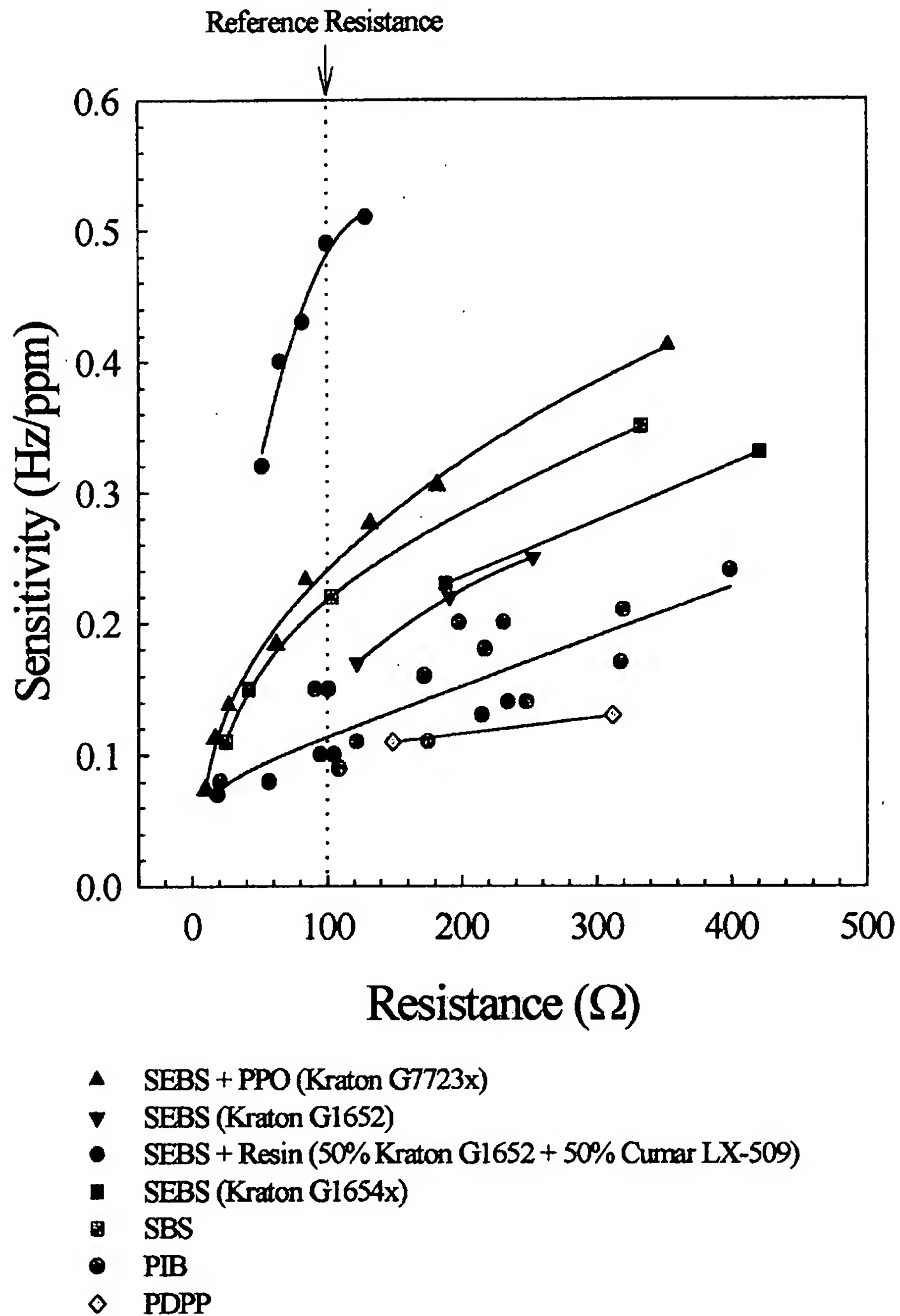


Figure 3. Sensitivity of various coatings to toluene at 50 °C as a function of resistance, demonstrating improved sensitivity of block copolymer coatings compared to the homopolymer coatings PIB and PDPP.

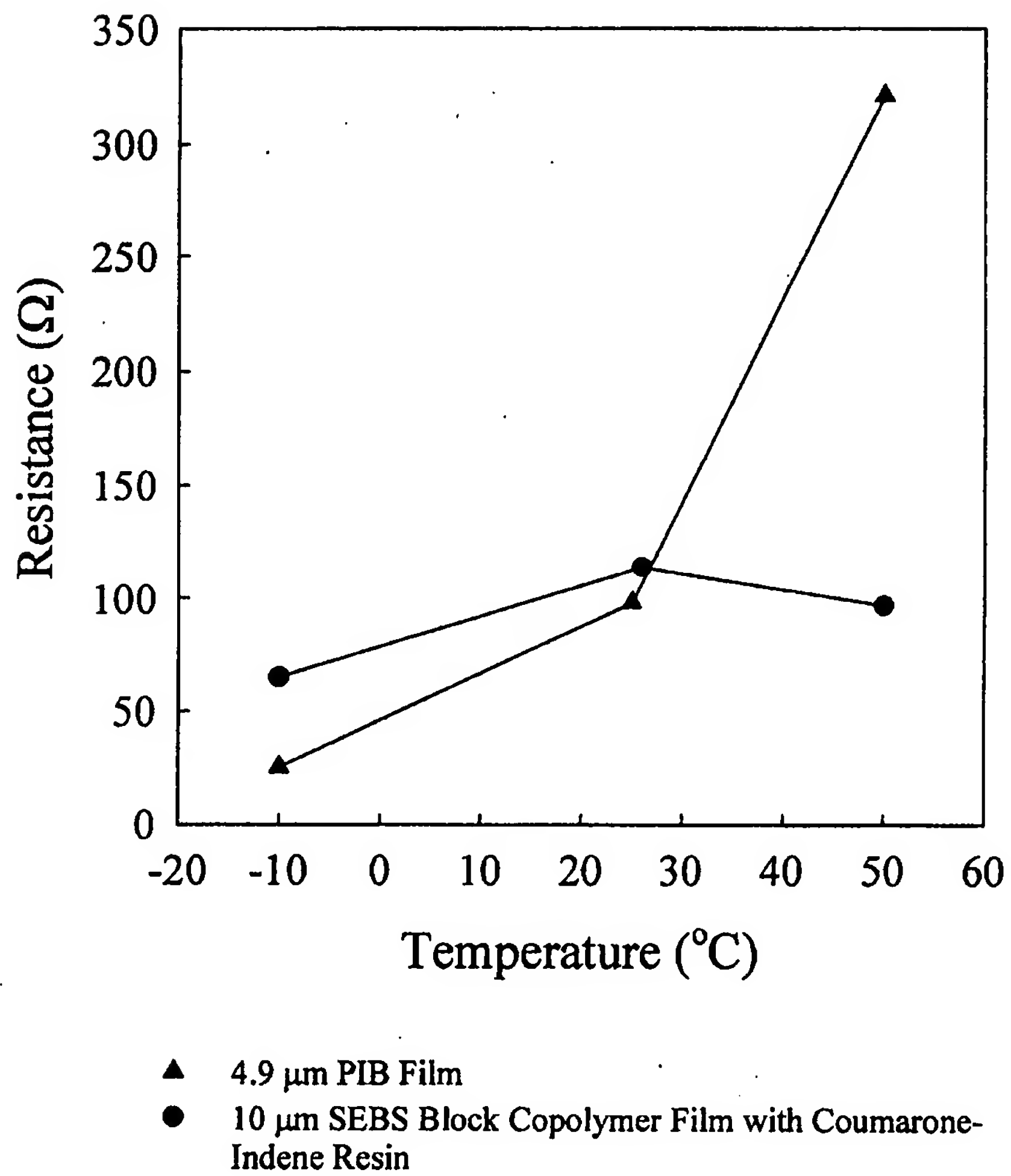
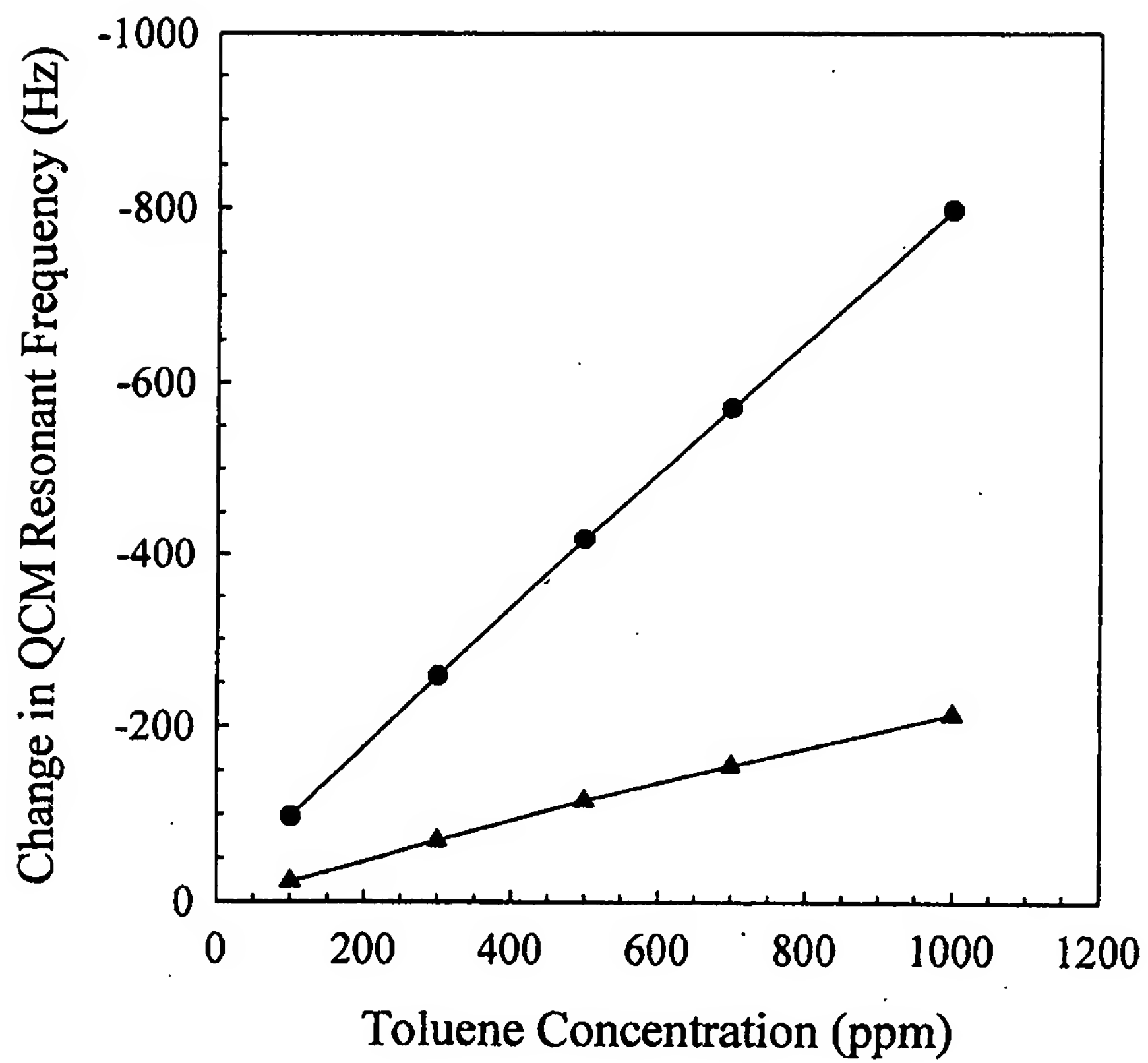


Figure 4. Comparison of the effect of temperature on the film resistance of a block copolymer coating vs. a homopolymer coating.



- ▲ 4.9 μm PIB Film
- 10 μm SEBS Block Copolymer Film with Coumarone-Indene Resin

Figure 5. Calibration curves for toluene sensors operating at 50 °C demonstrating the improved sensitivity of the block copolymer based film.

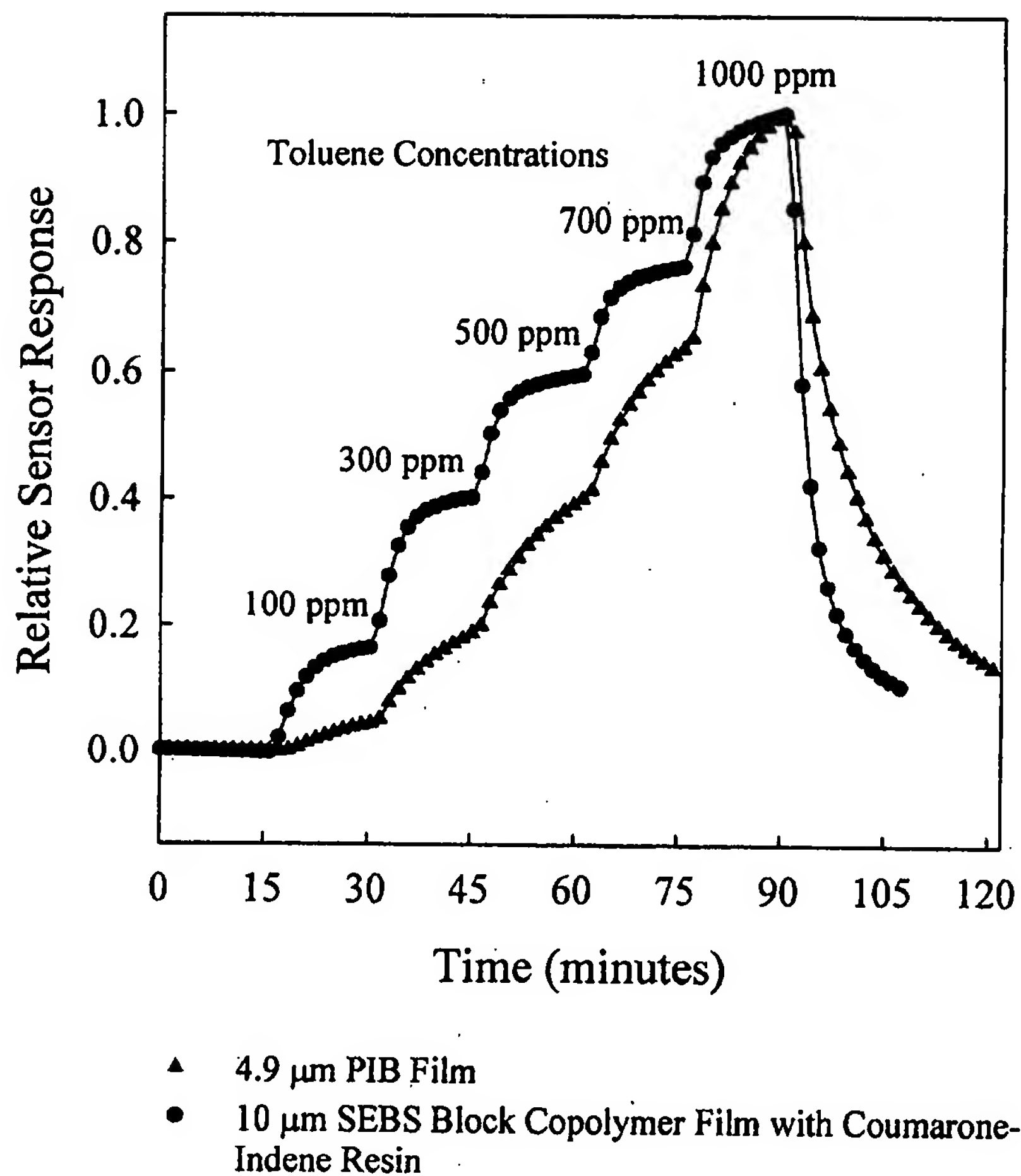


Figure 6. Comparison of the response times of toluene sensors coated with a homopolymer film and a block copolymer based film, operating at -10°C . The responses of each sensor have been scaled to the maximum response to 1000 ppm toluene in 15 minutes to facilitate comparison. The faster response of the block copolymer film is apparent.

